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SECOND ALL-UNION CONFERENCE ON RADIATION CHEMISTRY

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- USSR -

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[Following is the translation of an article by A. S. Kuz'minskiy and L. A. Oksent'yevich in Kauchuk i rezina (Synthetic and Natural Rubber), No 1, Moscow, 1961, pages 53-55.]

In Moscow on 10-14 October 1960, the Second All-Union Conference on Radiation Chemistry was held under the auspices of the Academy of Sciences USSR and the State Committee of Council of Ministers USSR on Chemistry.

Academician A. P. Vinogradov, who opened the conference, stated that radiation chemistry in recent years has become an independent branch of knowledge, which has a great future in the peaceful application of atomic energy. The development of radiation chemistry is proceeding in two basic directions: 1) industrial use of nuclear radiation and 2) more fundamental theoretical investigations of chemical conversions which take place under the influence of nuclear radiation.

The chairman of the organization committee of the conference, N. A. Bakh, emphasized in his introductory address the great significance of radiochemical investigations, both for the creation of radiostable material and for the use of nuclear radiations for carrying out controlled chemical processes. The possibility of carrying out a process of radiation polymerization at low temperatures is of great interest.

Deputy Chairman of the State Committee of the Council of Ministers USSR on Chemistry, G. V. Uvarov, described the radiochemical processes that will be introduced into industry as most promising. These include: 1) radiation polymerization of ethylene; 2) radiation vulcanization of special rubbers; 3) telomerization. They will be introduced into industry only where the application of nuclear radiation give a definite increase (in the case of low-energy processes when the reactions result in a long-chain yield) or when materials are obtained with improved or unique properties (in the case of radiation vulcanization of special rubbers and polyethylene).

The conference was held in five sections:

I. The effect of radiation on aqueous solutions.
II. The effect of radiation on organic substances.
III. Radiation polymerization and the effect of radiation on

polymers.
IV. The effect of radiation on solids.
V. Methodological problems in radiochemical investigations.

Between the sections, two sessions were held on theoretical questions of radiochemistry. In all, 120 reports (from about 35 institutes) were read at the conference.

Following is a brief listing of the most important reports which were heard at the section on radiation polymerization and the effect of radiation on polymers.

Radiation Polymerization

A. D. Abkin's report gave a short description of the process of radiation polymerization. It was mentioned that the major attainments in this area are the discovery of possibilities for carrying out polymerication at low temperatures, wherein the process proceeds by an ion mechanism. Several questions of radical polymerization were clarified in the report, as well as polymerication in emulsions and ion polymerization in the liquid phase. In radiation polymerication which proceeds by a radical mechanism, the same basic kinetic regularities are observed as in the usual methods of polymerization. The difference are apparent only for advanced stages of the reaction and with small magnitudes of radiation dosage. The basic features of radiation polymerization of ethylene were given. For the process of radiation polymerization in emulsion the general rate of polymerization was found to be independent of temperature and after-effects, and there was a lower activation energy and higher initiation rate than for polymerization in the bulk material. The problem of ion polymerization in the liquid phase was considered in detail. When isobutylene is irradiated at 0° no polymerization is observed, but at temperatures of -70° and below practically the same polymer is formed as in the case of ordinary initiation methods. Diphenylpicrylhydrazil does not inhibit the polymerization process. The rate of initiation in the bulk is small. Powdered additives (zinc oxide and others) have a pronounced effect. The rate of polymerization is proportional to the first power of the radiation intensity, which is characteristic of ion polymerization.

Later in the report, cases were examined of the joint polymerization of isobutylene and vinylidene chloride, styrol and methyl methacrylate. It was observed that the rate of polymerization of styrol in a solution of ethyl chloride under the influence of gamma radiation passes through a minimum upon lowering the temperature, and at low temperatures styrol polymerizes by an ion mechanism. Acrylonitrile may be polymerized by radiation in solvents which are electron donors. The surface plays a unique role during ion polymerization.

The report of Yu. L. Khmel'nitskiy, Ye. M. Kononova, and V. V. Nesterovskiy was devoted to radiation polymerization of propylene, isobutylene, and one of the amylenes (2-methylbutene-2) under various temperature conditions and with various monomer purities. It was

demonstrated that upon lowering the temperature and increasing the degree of purity for the monomer, the polymer yield is increased and their average molecular weight increases sharply. Polyisobutylene obtained by radiation methods differs from the product obtained by catalytic polymerization by a small content of low-molecular fractions, which is very significant during its application as a constituent of resins. It is hoped in the future to set up a large installation for carrying out radiation polymerization.

The work of I. P. Barkalov, A. A. Berlin, V. I. Gol'danskiy, B. G. Dzantiyev, and others was directed toward studying the kinetics and mechanism of radiation polymerization of acetylene hydrocarbons (phenylacetylene, cyclohexylacetylene, hexyne, and octyne). A number of regular patterns were established that differ from those known to exist for vinyl polymerization. To explain the results obtained, the authors postulated a mechanism which is related to the specific property of highly conjugated polymerization products (pronounced delocalization of unpaired electrons).

The communication of Ye. V. Volkova, A. F. Fokin, A. D. Sorokin, and V. M. Belikov on the problem of radiation polymerization of trifluorchlorethylene and tetrafluorethylene demonstrated that radiation polymerization of trifluorchlorethylene in the bulk proceeds easily. The polymer obtained has properties that meet the essential requirements.

Investigations were made of certain characteristics of the polymerization of tetrafluorethylene under the action of gamma and beta radiation with different radiation dosages, temperatures, and in different media. Polymerization in the bulk under the influence of gamma radiation takes place easily with a high yield (10^5 molecules/100 ev) and the speed of the process increases with the temperature and radiation dosage. Complete conversion takes place with dosages of the order of 10^5 r. A radical mechanism was proposed for the process. Upon carrying out the process of polymerization in a medium of chloroform, the speed of the process and the properties of the polymer obtained varied depending on the monomer concentration and radiation dosage. At the present time studies are being made of the kinetics of the process in the gaseous phase under the influence of beta radiation of Sr^{90}.

A series of reports were devoted to the acquisition of grafted copolymers under the influence of radiation. Kh. Y. Ysmanov, U. N. Musayev, and R. S. Tillayev carried out copolymerization of acrylonitrile with sylvan (methylfurane) and grafted copolymers were obtained from the systems: polyvinylchloride--acrylonitrile, polyvinylchloride--sylvan, perchlorvinyl--sylvan, and the properties of the resultant copolymers were investigated. R. S. Klimanova, V. I. Serenkov, and N. S. Tikhomirova investigated the cold polymerization of grafted styrol and polyethylene. A relationship was established between the degree of grafting and properties of the copolymers, and the conditions of radiation. The copolymers obtained can be used for ion-exchange membranes. In the future a continuous process is anticipated, as well as the development of increased facilities for carrying out this task.

The communication of V. L. Tsetlin, S. R. Rafikov, L. I. Plotnikov,

and P. Ya. Glazunov on radiation grafting of different polymer chains (polyvinylchloride, polyacrylonitrile, polymethylmethacrylate) onto the surface of mineral particles (magnesium oxide, powdered silica gel) and also onto carbon black was of interest. It was established that it would be possible in principle to carry out such a process leading to the modification of the surface of the indicated substances without destroying them. The grafting was carried out under the action of high-speed electrons in a special thermostatic chamber into which the monomer vapors were fed.

Effect of Radiation on Polymers

A report by V. L. Karpov and Yu. S. Lazurkin gave a general description of the processes that take place in polymers under the action of nuclear radiation.

L. G. Gurvich developed the theory of radiation destruction of linear polymers, on the basis of which he presented a solution of the kinetic equation of radiation destruction of linear polymers, a solution that was exact and still suitable for application. The dependence of the strength of the polymer fiber on variation in molecular-weight distribution during destruction was calculated.

A series of papers was devoted to the mechanism of radiochemical conversions in polymers. The method of electron paramagnetic resonance was used to study the kinetics of recombination of the fluoralkyl and peroxide radicals formed in teflon under the action of gamma radiation from Co^{60} (report by Yu. D. Tsvetkov, Ya. S. Lebedev, and V. V. Voyevodskiy), to investigate the radicals that appear upon irradiation of various oriented polymers in a nuclear reactor and in a beta-source (report by A. G. Kiselev, M. A. Mokul'skiy, and Yu. S. Lazurkin), and to investigate the influence of impurities (CCl_4, benzene, toluene, CS_2) on the linking of radicals in paraffin and polyethylene under the action of fast electrons. In the last paper N. Ya. Buben, A. T. Koritskiy, and V. N. Shamshev showed that even at low temperatures impurities and the radicals formed from them take an active part in the radiochemical effects, which may be explained on the basis of the notions of energy and charge transfer to the additive molecules. N. A. Slovokhotova, A. T. Koritskiy, and others used infrared spectroscopy techniques to study the structure of polyethylene irradiated in liquid nitrogen by fast electrons. V. G. Nikol'skiy and N. Ya. Buben studied the thermoluminescence of polyethylene, paraffins, teflon, synthetic rubbers, and certain aromatic hydrocarbons irradiated by fast electrons, in the hope of clarifying the structural transitions in these compounds.

A report by G. P. Ushakov, Yu. S. Lazurkin, and Yu. A. Gushcho was concerned with the influence of the phase state of polyethylene, at low pressure and irradiated in a reactor, on its physical and mechanical properties. Upon irradiation of polyethylene in a melt the cross links formed establish an irregular chain structure and inhibit crystallization. With increasing density of the space lattice the crystallinity falls off and the dimensions of the crystallites decrease

until a rigid noncrystallized mass is formed. Upon irradiation in the crystalline state even a close-packed lattice does not undergo complete crystallization.

V. L. Karpov, S. S. Leshchenko, and E. E. Finkel' studied the effect of various additives on the strengthening properties of polyethylene irradiated by a Co^{60} source in the process of thermal aging. It was shown that tin dibutylmaleinate, tin dibutyldistereate, and powdered silica gel (type A) exert a stabilizing influence. Dinaphthylmethane to a considerable extent preserves the relative elongation of polyethylene in the irradiation process. Consequently, the introduction of certain additives promotes an appreciable increase in the period of service of wires with irradiated polyethylene insulation at high temperatures.

Several reports were devoted to the effect of irradiation on synthetic rubber. In a paper by B. A. Dogadkin, Z. N. Tarasova, N. Ya. Kaplunov, and others the effect of sulfur on the kinetics of the radiation synthesis of natural and butadiene-styrene rubbers and the properties of irradiated vulcanized rubbers was studied. The authors noted appreciable bonding of sulfur to rubber during the process of irradiation, increased temperature enhancing the bond. The energy of activation of the radiation synthesis of synthetic rubber and its mixtures with sulfur is identical. In natural rubber at a temperature higher than 50° synthesis becomes reversed, whereas in the presence of sulfur this effect is not observed below 100°. Upon irradiation of a mixture of natural rubber and sulfur in an argon atmosphere the drop in unsaturability becomes less pronounced than in rubber alone. Sulfur-containing irradiated vulcanized rubbers possess higher strengthening properties, especially under high temperature conditions. The heat resistance of these vulcanized rubbers, however, is slightly lower.

B. A. Dogadkin, V. I. Gol'danskiy, Z. N. Tarasova, M. Ya. Kaplunov, and others developed a procedure for vulcanizing different samples of rubber on a linear pulse accelerator and studied the kinetics in the formation of the cross links and structural variations of natural, butadiene-styrene, and carboxylate rubbers upon irradiation by a beam of 2-Mev electrons. A comparison was made of the properties of vulcanized rubbers obtained under the action of gamma radiation from Co^{60} (dose power of $1.6\text{-}2.1.10^{-4}$ Mr/sec) and an electron base (0.2-0.8 Mr/sec). Vulcanized carboxylate rubbers have a higher thermalmechanical stability when irradiated by electrons. Evidently, with such high radiation intensities destructive processes cannot occur.

An extremely interesting paper was presented by I. Ya. Poddubnyy and S. V. Aver'yanov on the radiation vulcanization of siloxane rubbers, whereby the conditions of vulcanization of the various polysiloxanes are chosen so as to ensure a resultant rubber with very high thermal stability. It was found that the introduction of a number of heavy metals into the rubber and oxide charger mixture would enable one to obtain irradiated vulcanized rubbers retaining satisfactory physical-mechanical criteria after thermal aging at 300° for a one-month period, at 330° for five days, and at 370° for several hours. These irradiated vulcanized

rubbers have good physical-mechanical characteristics, surpass previously obtained rubbers considerably in thermal stability in a closed system with increased pressure, and have much less residual compressive strain at temperatures from 150 to 300°. The paper also considers the possible mechanism of increased thermal stability in irradiated vulcanized rubbers obtained in the presence of heavy metal compounds and discusses the problem of bond strength in irradiated vulcanized silicon rubber.

A report by A. S. Kuz'minskiy, L. S. Fel'dshtein, E. V. Zhuravskaya, and L. I. Lyubchanskaya was devoted to the principal regular patterns in the radiation aging of deformed rubbers made from the commercial types NK, SKS-30, SKB, and SKN-26. The kinetics of stress relaxation, rate of storage of residual compressive strain, and variation in equilibrium modulus were studied. This made it possible to distinguish between the simultaneously unfolding processes of destruction and synthesis and to evaluate them quantitatively. It was determined that vulcanized rubbers made from various rubber bases having the same vulcanizing group and order of increase of rate of destruction are distributed in the following series: SKN, SKS-30, SKB, NK. Upon thermal aging of rubbers made from types NK, SKN, and SKB the small difference in rates of destruction and synthesis leads to the curve of descending stress becoming the mirror image of the curve for storage of residual deformation. In the case of radiation aging this mirroring is upset because of the predominance of the synthesis process. The authors assume that the destruction and synthesis processes according to two, mutually independent and unrelated mechanisms. They investigated the influence of certain additives (antiradiants) and medium (air, vacuum) on the kinetics of stress relaxation upon irradiation. It was shown that upon irradiation in vacuum with tensile strain and in air with compressive strain the introduction of antiradiants does not affect the rate of destruction. The investigated antiradiants greatly lower the rate of synthesis of the rubber under the influence of radiation.

G. A. Blokh, V. L. Karpov, Yu. M. Malinskiy, L. P. Ol'shanskiy, and M. S. Khloplyankina studied the action of gamma radiation from Co^{60} on assorted cable rubbers and structures. It was established that after irradiation with a dosage of 50-100 Mr the fundamental physical-mechanical and electrical insulating properties of cable rubbers and structure deteriorate. Type TS-35 insulation rubber (made from types NK and SKB) is more stable against the simultaneous effect of heating (70°) and irradiation with a dosage of 50 Mr for 70 hr than type ShN-40 hose rubber (from chloropene rubber).

In the interim sessions lively discussions were held on papers relating to the theoretical problems of radiation chemistry. The questions of radiation energy distribution and transfer in organic systems and the mechanism of radiochemical processes were considered.

At the closing session the work of the conference was summarized. It was remarked that the three years which passed since the first conference had convened were marked by: 1) a substantial over-all growth in radiochemical research, as evinced by the number of papers read and number of delegates present at the conference; 2) a considerable

expansion in the study of the general theoretical nature and in the study of the mechanism of radiochemical processes, based on the expansion of experimental research; 3) the appearance of a large number of published papers on the effect of radiation on the solid state; 4) the application of new physical and composite methods for research, such as the method of electron paramagnetic resonance (more than 20 papers), chromatographic, electrical, spectral, and other methods. All this is a sign of the further increase and refinement of work in radiation chemistry.

It was resolved to hold a conference on the industrial application of radiochemical processes in 1961, in 1962 a conference on the general theoretical problems and problems of the mechanism of radiochemical processes, and in the fall of 1965 the Third All-Union Conference on Radiation Chemistry.

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